Nitrogen Loading Criteria For Estuaries In Prince Edward Island

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NITROGEN LOADING CRITERIA FOR ESTUARIES IN PRINCE EDWARD ISLAND

by

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ABSTRACT

Bugden, G., Jiang, Y., van den Heuvel, M.R., Vandermeulen, H., MacQuarrie, K.T.B., Crane, C.J. and B.G. Raymond. 2014. Nitrogen Loading Criteria for Estuaries in Prince Edward Island. Can. Tech. Rep. Fish. Aquat. Sci. 3066: vii + 43 p.

As part of efforts to develop nitrogen criteria for estuaries a simple loading model, based on the principle of a Continuously Stirred Chemical Reactor, has been developed for Prince Edward Island. Nitrate loading and flushing characteristics for thirty four Island estuaries have been used to calculate values (Δ**N** or Delta-N) that represent the theoretical nitrate concentration that would exist in each estuary in the absence of biology and chemical or physical processes.

The model shows remarkably good correspondence to the oxic condition of most of the thirty four estuaries to which the model was applied; twenty six of thirty four estuaries had Δ**N** values that correctly indicated whether these estuaries had experienced any anoxic events in the ten years between 2002 and 2011. Chlorophyll and dissolved oxygen data from the PEI Estuaries Survey has been used to validate model outputs and confirm these findings.

RÉSUMÉ

Bugden, G., Jiang, Y., van den Heuvel, M.R., Vandermeulen, H., MacQuarrie, K.T.B., Crane, C.J. and B.G. Raymond. 2014. Critères relatifs à la charge en azote pour les estuaires de l'Île-du-Prince-Édouard. Can. Tech. Rep. Fish. Aquat. Sci, 3066: vii + 43 p.

Dans le cadre d'efforts visant à établir des critères relatifs à la charge en azote pour les estuaires, un simple modèle de charge, fondé sur le principe d'un réacteur chimique à brassage continu, a été mis au point pour l'Île-du-Prince-Édouard. Les caractéristiques de charge en nitrate et de lessivage associées à trente-quatre estuaires de l'Île ont servi à calculer les valeurs (Δ**N** ou Delta-N) qui représentent la concentration théorique en nitrate qui serait présente dans chaque estuaire en l'absence de processus biologiques et chimiques ou physiques.

Les résultats du modèle correspondent remarquablement bien aux conditions oxiques de la plupart des trente-quatre estuaires auxquels le modèle a été appliqué; vingt-six des trente-quatre estuaires avaient des valeurs Δ**N** qui indiquaient correctement si les estuaires avaient connu ou non des activités anoxiques dans la période de dix ans allant de 2002 à 2011. Des données sur la chlorophylle et l'oxygène dissous tirées du relevé des estuaires de l'Île-du-Prince-Édouard ont permis de valider les produits du modèle et d'en confirmer les résultats.

INTRODUCTION

Eutrophication caused by nutrient enrichment is one of the leading causes of water quality impairment within coastal marine environments (NRC, 2000). Eutrophication in coastal systems is manifested as the occurrence of toxic or nuisance phytoplankton blooms, prolific growth of certain short-lived macro-algae species, loss of submerged aquatic vegetation, increased organic matter in sediments, depleted dissolved oxygen levels (hypoxia / anoxia), changes in aquatic community structure, fish and shellfish kills and the loss of recreational water use and aesthetic appeal (Nixon 1995; NRC 2000; Boesch 2002). These changes can have significant negative impacts on activities such as commercial and recreational fisheries as well as tourism and real estate development. Eutrophication is a widespread phenomenon which has been recorded in coastal areas in virtually every corner of the world (Nixon 1995; Selman et al. 2008).

Eutrophication of near-shore marine areas in Prince Edward Island (PEI) is a significant issue. Fourteen Island estuaries have experienced anoxic events in at least four of the last five years (Figure 1) and more than forty different estuaries have had at least one anoxic event since 2001.[1] In PEI an anoxic event is defined as a condition where oxygen is completely depleted and areas of discolored and foul (sulfur) smelling water are present (Figure 2). However, no attempt is made to define the spatial extent or duration of the event. Most of these events are located on the northern or southeastern shores of PEI (Figure 1) where lower ambient tidal ranges, and the subsequent reduced flushing, may make estuaries more susceptible to eutrophication. Many Island estuaries are also affected by the prolific growth of *Ulva* (sea lettuce, Figure 3), other ephemeral macro-algae and / or phytoplankton blooms.

There was an urgent need to address these environmental concerns in PEI. Government and the public alike were asking for ways to address the issues of prolific sea lettuce growth and widespread anoxic events in the province (PEI ELJ 2008). While it was widely known that eutrophication and its symptoms, including anoxia, are best addressed by reducing the supply of nutrients that drive the process (Nixon 1995; Valiela et al. 1997; NRC 2000; EPA 2001; Boesch 2002) managers and stakeholders alike had a need to know, in an informed way, how much of a reduction in nutrient loading was required in order to meet certain water quality objectives. Since rehabilitation efforts were likely to involve significant changes in land management it was necessary to determine the proper scale of response required for affected systems. An appropriate science-based approach to develop nutrient criteria was needed. This was examined through comparison of nitrogen loading data to the presence and absence of anoxia taking into consideration appropriate corrections for tidal flushing. The criteria produced are intended to guide watershed nutrient planning efforts in PEI.

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[1] The province posts this information:
http://www.gov.pe.ca/environment/index.php3?number=1035882&lang=E

Project Background

The Canadian Council of Ministers of the Environment (CCME 2007) developed a guidance framework for the development of nutrient criteria for near-shore marine areas, which is based on an approach developed by the United States Environmental Protection Agency (EPA 2001). As per the guidance framework, the province of PEI established a small Regional Technical Advisory Group (RTAG) made up of a panel of regional and local experts in estuarine ecology, macro-algae growth, nutrient loading, fresh water hydrology and oceanography[2]. The RTAG was tasked, by the province of PEI, to develop a science based approach that would be used to develop nutrient criteria for PEI's estuaries. To expedite the process the RTAG was asked to use only data that was currently available and / or new data that could be quickly and easily collected.

An initial question for the RTAG was identifying which nutrient or nutrients should be considered for the establishment of nutrient criteria in PEI. While nitrogen and phosphorus are the two elements commonly indicated as controlling eutrophication in aquatic systems, nitrogen is widely accepted as the limiting element in estuarine systems (Nixon 1995; Valiela et al. 1997; NRC 2000; EPA 2001; Howarth and Marino 2006). In PEI a case can be made for nitrogen, primarily from nitrate based fertilizers, as the causal element for estuarine eutrophication. Dixit and Brylinsky (2008) demonstrated that measures of estuary trophic status were better represented when nitrogen, rather than phosphorus, loading was used in their susceptibility index. Nitrate is the most common form of nitrogen in freshwater in PEI (Somers et al. 1999) and long-term fresh water monitoring in the province shows significant upward nitrate trends over the last several decades (Environment Canada 2011; Figure 4). These trends increased during the early to mid-1990s, a period in which significant changes in agricultural land use occurred (Figure 4). In contrast, total phosphorus concentrations have shown little or no upward trend over the same period (Environment Canada 2011), are not correlated with the level of agriculture in watersheds, and have been found to be more strongly associated with geological gradients on PEI (van den Heuvel 2009).

Estuaries are complex systems that have highly variable biological processes and interactions (Cloern 2001; Boesch 2002; Nixon 2009). While it may be argued that these complex interactions need to be ascertained to fully understand a estuary's response to eutrophication and to plan comprehensive rehabilitation, simple approaches based on susceptibility to inputs can be a suitable first step in determining required nutrient reductions (EPA 2001; Boesch 2002). Dixit and Brylinsky (2008) have shown that a susceptibility-based approach held promise for Island estuaries. The RTAG hypothesized that such a susceptibility-based approach could be developed, utilizing the currently available but limited data for PEI, to establish interim nitrogen targets that would be

[2] The authors of this report include the full RTAG membership plus those closely associated with the group.

sensitive enough to establish the magnitude of nitrogen reductions required in specific systems. These targets would be further refined as additional data became available.

Dixit and Brylinsky (2008) hypothesized that the degree to which estuaries are susceptible to nutrients is a function of their nutrient loading and ability to flush and dilute those nutrients. Estimates of nutrient loading, flushing and dilution potential were used to create an index which demonstrated promising potential for the development of nutrient criteria (Dixit and Brylinsky 2008).They concluded that their approach could be improved by using more specific estimates of nutrient loading.

Like Dixit and Brylinsky (2008), the RTAG reasoned that nutrient (in this case nitrogen in the form of nitrate) loading was the most appropriate causal factor in the development of eutrophic conditions in Island estuaries. Ambient concentrations in contributing freshwater streams did not have any relationship to the presence of anoxia in any given estuary and did not reflect the total amount of nitrogen entering the estuaries from this source (Raymond et al. 2002). Although nitrogen loading data were not directly available for most estuaries, the RTAG reasoned that nitrogen loading could be modelled using available information on land use and existing groundwater and surface water data to validate model outputs.

The RTAG also agreed with Dixit and Brylinsky (2008) that tidal flushing was an important factor in determining a particular estuary's susceptibility to nitrogen loads. There was some evidence to support this as north shore PEI estuaries (with a mean tide range of just 0.7 m) had noticeably higher occurrence of anoxic events than south shore estuaries (with ranges of 1.2 to 1.9 m, Figure 1). Flushing was also a physical characteristic that could be calculated using available resources.

The process of developing a simple nitrogen loading model, that captured these elements of loading and flushing, as well as the interim nitrate targets that were developed as a result of this model - are described in this document.

2.0 MODEL DATA COLLECTION

2.1 Biological Responses and Endpoints

The RTAG selected anoxic events as the chief response variable for the development of nitrogen criteria. The process of eutrophication was viewed by the RTAG as a gradient of increasing primary productivity cumulating in anoxic events (Figure 5). While potential water quality targets could be selected from anywhere along this gradient the RTAG recognised that assigning targets based on other indicators of productivity would be challenging given limited data availability; Chlorophyll had previously been shown to be an inadequate measure of productivity in the benthic macroalgae dominated estuaries in PEI (Meeuwig

1998; Martec Ltd. 2002; Raymond et al. 2002) and data for macroalgae productivity or eelgrass decline were not available.

The RTAG theorized that reducing or eliminating anoxic events would effectively reduce productivity, by an unknown factor, while addressing anoxia (Figure 5) the water quality issue of greatest public concern. The RTAG also assumed that future refinements and iterations of nitrogen criteria for PEI estuaries would incorporate more specific productivity targets once productivity measurements became available.

The Prince Edward Island Department of Environment, Labour and Justice (ELJ) has been compiling a record of the occurrence of anoxic events in the province since 2002[3]. Anoxic events were reported to ELJ by members of the public, staff of other federal or provincial departments or were from observations or reports from ELJ's own staff. These events have mostly been confirmed by taking dissolved oxygen (DO) readings in the field; however, this was not done in all cases. In some instances, such as where there is an annual history of anoxic events, DO readings were not made. ELJ has assigned estuaries that have had at least one anoxic event a status of "Anoxic" and those that have had no reported events a status of "Non-Anoxic". While this list is considered by ELJ to be reasonably complete it is acknowledged that some anoxic events may go unreported and / or unobserved. The assignment to either status also does not consider either the spatial extent (some reported events were very small and some quite large) or the duration of reported events, which could be used as a measure of intensity of anoxic events.

The RTAG recognised that the assignment of particular estuaries as either "Anoxic" or "Non-Anoxic" was a binary endpoint that would provide little interpretation of model outputs. In the absence of productivity measurements additional data representing estuary response variables were also considered in order to provide model validation.

The PEI Estuaries Survey is an annual survey of 25 Island estuaries. It was designed as a long-term survey of eutrophication indicators in Island estuaries (Shaw 1998). Twenty one sites have been sampled since 1999, with the rest being added in recent years[4]. The survey is conducted over a three week period from late July to early to mid-August. This time frame was chosen as it was the time of year when anoxic events were most common in 1998 (Shaw 1998). Although the onset of anoxic events has shifted to earlier in the season in recent years, this sample timing has been retained.

Three sites are sampled in each estuary at upper, middle and lower estuary locations[4]. These three stations represent a gradient of salinities from the uppermost area that was accessible by boat to the outer or lower area which marked the transition from estuary to open water or coastal embayment. Although mean chlorophyll and salinity values were considered when three sites

[3] The province posts this information : http://www.gov.pe.ca/environment/index.php3?number=1035882&lang=E

[4] Sample sites are listed by the province: http://www.gov.pe.ca/photos/original/elj_estuary_sv.pdf

in each estuary were chosen, more emphasis was placed on choosing sites that were in comparable upper, middle and lower geographical locations than on the similarity in these parameters (Shaw 1998).

Measured parameters at each site include water temperature, salinity, specific conductivity and dissolved oxygen. A YSI 85 handheld multi-meter was used for all measurements. Sampled parameters include nitrate (flow injection analysis colorimetry; PEIAL 2011b), total nitrogen (in line digestion and flow injection analyses; PEIAL 2012a) and total phosphorus (flow injection analysis; PEIAL 2012b) and chlorophyll-a (fluorometry; PEIAL 2011a). All samples were analysed by the PEI Analytical Laboratories.

Samples and measurements are taken from both the upper (0.3 m from the surface) and lower (from 0.3 to 0.5 m above the bottom) portion of the water column. All data are currently stored in provincial water quality databases and are available to the public[5].

Dissolved oxygen and chlorophyll can be considered response variables. As estuaries become eutrophic, dissolved oxygen values measured during daylight hours (when discrete measurements for the PEI Estuaries Survey are made) may be elevated as phytoplankton and benthic macroalgae produce oxygen through photosynthesis. In estuaries that experience anoxic events daytime dissolved oxygen levels could also be low to very low or nil if an event is occurring at the time of sampling. As a result, dissolved oxygen measurements from eutrophic systems can be highly variable. The RTAG hypothesized that this variability could be used as response variable to validate model outputs.

The RTAG hypothesized that primary productivity in PEI estuaries could be best characterized by the biomass of *Ulva* present. Macroalgae can be the dominant primary producer in shallow temperate estuaries (Valiela et al. 1997). However, the productivity of *Ulva* growth in PEI estuaries had not been well documented and was not available for use as a response variable.

Chlorophyll-a is generally used as a proxy for estuarine productivity in marine systems (EPA 2001). However, in PEI estuaries chlorophyll levels did not appear to represent the complete picture of productivity (Meeuwig 1998; Martec Ltd. 2002; Raymond et al. 2002) likely due to the large biomasses of *Ulva* present. Phytoplankton blooms also do not appear to be strongly related to anoxic events as the highest chlorophyll concentrations are associated with phytoplankton blooms that occur after an anoxic event as nutrients are released to the water column (Schein et al. 2012). The RTAG hypothesized that chlorophyll concentrations would, however, provide an indication of the degree of eutrophication present as concentrations should rise as nutrient (in this case nitrogen) inputs increase (Valiela et al. 1997).

Data from the PEI Estuaries Survey from for 2002 to 2011 was used to test these hypotheses. Data for the PEI Estuaries Survey are not collected at a specific tidal stage and results tend to be highly variable for both dissolved oxygen and

[5] http://maps.gov.pe.ca/mapserver2012/PEI_Maps/Public_Water/waterdata/tool.php.

chlorophyll due to tidal exchange. To eliminate some variation in results, only data collected during mid-tide (either flood or ebb) was used for analysis. This produced 12 to 15 data points for each site in the survey.

Mean dissolved oxygen values were very similar at both the outer and middle estuary stations in both anoxic and non-anoxic estuaries (Figure 6). Dissolved oxygen saturation values were lower at the upper station in anoxic estuaries than in non-anoxic estuaries but by a margin that was less than what might have been expected. Estuaries known to experience anoxic events also had a wider variation in dissolved oxygen saturation than non-anoxic estuaries (Figure 6).This variation is likely a result of estuary condition at the time of sampling. If the estuary was undergoing active algal growth, very high to super-saturated (levels above 100% saturation) dissolved oxygen values would have been present - but if the estuary was undergoing a collapse or die off of algal biomass hypoxia or anoxia (levels below 100% saturation) would have been observed. Non-anoxic estuaries may display less variation in dissolved oxygen saturation due to lower productivity resulting in fewer extreme values (Figure 6).

Chlorophyll-a concentrations were found to be similar at the outer estuary station for both anoxic and non-anoxic estuaries (Figure 7). Chlorophyll-a concentrations were higher in estuaries with known anoxic events at both the middle and upper estuary stations (Figure 7).

The RTAG also reasoned that modelling efforts should mirror the timing of the biological responses being observed in PEI estuaries. The occurrences of hypoxia / anoxia were anecdotally known to coincide with the die-off of very dense *Ulva* populations. In most PEI estuaries the accumulation of rotting sea lettuce on the shoreline and in the water column goes hand in hand with reports of anoxic events. Since anoxic events are not known to occur outside of the active growing period of *Ulva*, the RTAG postulated that the active growing season, which was considered to be May to October in PEI, should be considered in the development of nitrogen criteria. As a result the model that was ultimately developed was for the six-month period between May and October, referred to as 'Summer' in the nitrogen criteria model.

2.2 Loading Estimations

Nitrate is delivered to estuaries mainly through surface runoff and groundwater discharge (i.e. base flow). In general, very little nitrate is lost from agricultural landscapes via surface runoff (Jackson et al. 1973; Logan et al. 1994; Ramos 1996). This is because, assuming good soil structure and soils that are not already saturated, there will be sufficient infiltrating water to carry a significant portion of the nitrate to depths below where it will be vulnerable to losses via runoff (Baker 2001). Measurements of nitrate in runoff were limited in PEI but confirmed low concentrations of nitrate (Dunn et al. 2011). Although it is possible that significant nitrogen losses could occur if a major runoff event were to take place shortly after surface application of a nitrogen rich fertilizer (Smith et al. 1990), major runoff events usually occur in late fall, winter and early spring in PEI

and, as discussed above, nitrate loadings delivered to the estuaries during these seasons are not relevant to summer eutrophication and *Ulva* growth. As a result, nitrate loads delivered through runoff were not estimated in this exercise.

PEI is entirely underlain by an unconfined or semi-confined fractured-porous aquifer. Leached nitrate from non-point sources and point sources percolates through the vadose zone, enters the aquifer, and discharges with springs and seepage into the streams and associated estuaries. It has been estimated that groundwater-derived base flow accounts for about 60-70% of annual stream flow and 100% of summer stream flow in a typical PEI stream (Jiang et al. 2004). The nitrate load from groundwater discharge is therefore highly relevant to summer eutrophication and the estimation of this load is the focus of this work.

Nitrate loading to an estuary is a function of freshwater discharge and its associated nitrate concentration. Nitrate loading to an estuary includes discharges from both stream inflow and underwater springs and seeps in the estuary itself; and these sources of loading can be measured in some cases (Danielescu and MacQuarrie 2011). However, existing data was sparse or not readily available for PEI, so a land use-based model was developed for estimating nitrate loading to the estuaries through groundwater discharge (Nishimura and Jiang 2011). Briefly, the steps in the model development were:

1. land use within a study watershed was grouped into several categories using satellite imagery data;
2. annual leached nitrate concentration for each land use category was defined from either measurements or modeling;
3. annual leached nitrate concentration and the corresponding land use areas were used to calculate an area-weighted concentration;
4. annual nitrate loading from septic systems was estimated and converted into an equivalent leached nitrate concentration;
5. area-weighted concentration plus the equivalent leached nitrate concentration from septic systems integrated with average annual groundwater recharge (420 mm) yielded an annual nitrate load from groundwater discharge;
6. seasonal loads were calculated by assuming them proportional to the seasonal distribution of base flow;
7. where long-term discharge measurements were not available, annual base flow was prorated using annual base flow of a comparable hydrometric station.

Since data for a field-based assessment were lacking, LANDSAT and SPOT imagery data (2006 – 2009) were used for land use classification. Land use within a watershed was grouped into; agricultural land under potato rotation (A), agricultural land not under potato rotation (B) and forested areas (C). Group A was subdivided into two-year (A_1) and three-year (A_2) rotation types because rotation length influences nitrate leaching and grain crops were assumed to be in

rotation with potato crops for both Groups A_1 and A_2. The leached nitrate concentrations for Group A_1 and A_2 were standardized across PEI and approximately represented the cropping practices for the period of 2000-2010. Grass, pasture, forage, soybean and all crops other than potatoes and grains were grouped as Group B. Group C included all forested areas, urban lands, highways as well as recreational and commercial land use. The resolution of the imagery data and lack of field-specific management information did not support further refinement of land use classification.

Initial annual leached nitrate concentrations for each land use category were defined from measurements from tile drainage effluents, groundwater sampling, estimations and simulations using the LEACHN and groundwater simulations (Jiang et al. 2011; Jiang et al. 2012). Initial annual leached nitrate concentrations (volume-weighted) for Groups A_1 and A_2 lands were predicted as 10-14 and 8-12 mg N/L respectively, and the broader ranges of prediction reflected the variations of crop varieties, management practices and soil. Measured values for Group B were 1-3 mg N/L (Milburn 1998). Initial leached concentration for Group C, representing background groundwater nitrate levels in PEI, was estimated as 0.2-0.7 mg N/L. Manure inputs from livestock were not explicitly simulated in the LEACHN modeling but were assumed being credited as part of the nitrogen application for the simulated crops.

The nitrate concentration of precipitation was calculated using the atmospheric deposition rate of 3.7-6.3 kg N/ha estimated by Robert Vet (Environment Canada, personal communication, 2005) and annual precipitation of 1100 mm in PEI. These were used as input for LEACHN simulations. Therefore, the effects of atmospheric deposits and N contribution from atmosphere were reflected in the above estimations.

Nitrate loads from septic systems were estimated on a household basis using values provided by ELJ (Morley Foy, personal communication 2005). The total nitrogen concentration of septic effluent was assumed to be 40 mg/L (ammonia is assumed to convert to nitrate in the septic distribution field). Annual household water use was assumed to be 92 m^3 in summer and 158 m^3 in the other seasons. Since nitrate uptake by plants is assumed to be 20-30% in summer, the annual septic nitrate load was estimated as 10.4 kg N/y per household. This was very similar to the household load estimated in Massachusetts (Valiella et al. 2002).The number of households which were not on central waste water treatment systems in each watershed was estimated using provincial civic address data and a total estimated nitrate load was calculated. This loading was converted into an equivalent nitrate concentration using the average annual recharge (420 mm).

The area-weighted concentration plus the equivalent concentration of septic system loading was assumed analogous to the nitrate concentration of freshwater discharged to the estuary.

The above calculations can be summarized as:

$$N_{gw} = (C_{a1} \times A_{a1} + C_{a2} \times A_{a2} + C_b \times A_b + C_c \times A_c) / (A_{a1} + A_{a2} + A_b + A_c) + C_{eqv} \quad (1)$$

Where

N_{gw} is the leached nitrate concentration used in the loading calculation (M/L^3) (i.e. nitrate concentration of fresh inflow into the estuary)

C_{a1}, C_{a2}, C_b and C_c are leached concentrations of land-use groups A1, A2, B and C respectively (M/L^3)

C_{eqv} is the equivalent concentration of septic systems (M/L^3)

A_{a1}, A_{a2}, A_b and A_c are areas of land use groups A1, A2, B and C respectively (L^2)

The model outputs (i.e. annual leached nitrate concentrations) were calibrated against nitrate concentration measurements made in 27 tributaries in 2007 and 2008, and the leached nitrate concentration for each land use category was finely tuned through a trial and error approach. The calibrated model was also verified against summer-season nitrate concentrations measured at the outlets of 138 sub watersheds across the island (Nishimura and Jiang 2011).

During the calibration and verification processes, the predicted annual leached nitrate concentrations were also compared against average nitrate concentrations of domestic well water samples within the study watersheds. While the predicted nitrate concentrations compared closely with the measured nitrate concentrations of stream water, the predictions were about 1-1.5 mg N/L lower than the average concentrations of well water samples. The discrepancy is likely due to the fact that the averages of domestic well water samples may have been biased because the wells were impacted by septic systems and did not represent the watershed-wide shallow groundwater averages (Nishimura and Jiang 2011).

The calibrated and verified land use nitrate model was used to predict nitrate loads for the estuary nitrogen criteria model at 34 estuaries (Figure 8, Table 1). These estuaries were chosen because nitrate concentration data were available for the freshwater tributaries of these estuaries and could be used to ground-truth model outputs as described above.

Since a seasonal load estimate was required for this exercise it was necessary to determine the proportion of base-flow occurring between May and October. Hydrographs of monthly mean flow were developed for each of the five continuously monitored hydrometric stations in PEI using data for the period from 1963 to 2001. The monthly mean base flow was separated from each of the hydrographs. Since monitoring data (Jiang and Somers 2009; Danielescu and MacQuarrie 2011) indicated that nitrate concentrations of stream water in PEI were relatively constant in the lower portions of the watersheds over a year, monthly nitrate loads contributed by groundwater were assumed to be proportional to base flow.

Monthly nitrate loads from groundwater were calculated by multiplying the annual nitrate loads by the monthly percentage of annual base flow. Mean monthly base flows for streams in each of the 34 estuaries were prorated by applying the proportion of base flow occurring in that month at the closest hydrometric station to the total estimated annual base flow.

Stream flow measurements, taken between July and September in 2009 in several dozen streams from around the province, showed strong correlations to the discharges prorated from the existing hydrometric stations. This suggested that prorating base flow from the monitored hydrometric stations to the un-gauged streams was appropriate for nitrate loading estimation in the absence of long-term measurements (Nishimura and Jiang 2011).

It is noted that use of this modeling approach did not account for any attenuation in nitrate through denitrification or other processes. Stable isotope examination of groundwater in the Wilmot, PEI watershed indicated that very little denitrification occurred in the aquifer (Savard et al. 2007) and this was assumed to be case across PEI. The extent of denitrification and uptake in riparian zones and by in-stream processes was not known but was assumed to be negligible.

Point sources of loading such as municipal and industrial effluents were also estimated and were included if they represented loading to upper or middle estuary areas. Point sources to lower estuary areas, near the estuary / coastal boundary, were not considered as the RTAG reasoned that these loads would be quickly exported out of the estuaries. Municipal wastewater flows were estimated from the number of households served and loads were calculated using the available but infrequent measurements of total nitrogen concentrations. Typical concentration values, based on monitoring results, were assigned and used in daily load calculations.

Nitrogen loads from industrial effluents were taken from measured loadings also as total nitrogen. Estimated daily loading for both municipal and industrial effluents were scaled up to the six-month period, covering the period of active *Ulva* growth (May to October), considered in this exercise. The use of total nitrogen, which included both organic and inorganic forms of nitrogen, likely represents an over estimation of bio-available nitrogen from these sources. Despite this over-estimation these sources generally represent a relatively small proportion of total loading from both point and non-point sources (i.e. less than 5% of total N loading in most cases).

It should be noted that several simplifications, standardizations and assumptions were made in the loading estimations used here. Potential adjustments to estimation could be made with refinements to the model based on more complete data on cropping practices, soil properties and climate as well as the processes governing the transport of nitrate from the root zones.

Using the output from the loading estimations as input, groundwater nitrate transport and fate models could be developed to improve the understanding of the impacts of groundwater processes on nitrate delivery to the estuaries. Nitrate loadings contributed from run-off as well as from point sources could also be

estimated and incorporated into the loading estimations or a surface water model - which would be coupled to the groundwater model for inputs, and could be used to better capture stream loads.

2.3 Estimation of Estuary Flushing

In aquatic ecosystems it is essential to understand the hydrodynamic processes that transport water and its constituents (living biomass, nutrient mass, dissolved gases, etc.; Mansen et al. 2002). First order descriptions of this transport, such as flushing time, residence time, fraction of fresh water and age, are often used as measures of estuary dynamics (EPA 2001; Mansen et al. 2002, Sheldon and Alber 2006). Although the RTAG considered these first order models to be appropriate, these approaches generally require bathymetry, volume or tidal flow data which were not available for this exercise. Alternative methodology was needed.

The computation of flushing can be based on the assumption that a water body functions as a continuously stirred chemical (or tank) reactor (CSCR) (Mansen et al. 2002). In a CSCR, an estuary can be thought of as a closed vessel with constant inflow and outflow in which a constituent, such as a nitrogen load, is instantaneously mixed. This would result in a situation where the concentration of the constituent exiting the system is the same as the concentration everywhere within the estuary (Mansen et al. 2002).

Although this theoretical situation does not necessarily reside within the real world due to the presence of biological, chemical and physical processes that show substantial spatial variation within an estuary (Mansen et al. 2002), the RTAG theorized it might have application to the development of a simple model that can be used to define estuary susceptibility to nitrogen loads. The RTAG also theorized that the inflow and outflow rates could be considered over a long periods, such as the assumed six month growth period for *Ulva*, to arrive at this theoretical concentration in the vessel (estuary).

The tidal input volume for each of the thirty-four estuaries with loading estimates was calculated by multiplying the surface area of the estuary, measured to the seaward boundary, by the total amplitude of tide entering the estuary (Figure 9). The seaward boundary was defined as the line drawn across the mouth of the estuary at the point where there was enough of a physical change (widening or becoming less enclosed by land) so that ocean or bay conditions were likely present rather than estuary conditions. No physical measurements were used in this determination.

The total tidal amplitude represented the sum of the tide entering the estuary on flood tides over the period of May to October (Table 2). Where water level observations were available, the data was subjected to a tidal analysis to extract the various tidal constituents. A predicted tide signal was developed using the MATLAB T_Tide routine (Pawlowicz et. al. 2002). All extracted constituents with a signal to noise ratio greater than 2 were used to develop the predicted tide.

Where water level observations were not available, the five tidal constituents from the grid point of a numerical model (Dupont et al. 2002) were used to develop the predicted tide. The total volume of fresh water entering the estuary over the same period was taken from the freshwater flow estimates developed for the loading calculations. The time interval was once again the six month period of May-October; the assumed growing season for *Ulva*.

2.4 Model Development

The RTAG theorized that an increase in nitrogen concentration in an estuary above a certain limit or threshold would result in increased risk of eutrophication and anoxic events. The RTAG reasoned that, although there are variable tidal conditions and complicated and highly variable biological processes as well as multiple nutrient sources, sinks and reservoirs present in all estuaries, the eutrophication risk posed by loading could be characterized in very simple terms (EPA 2001; Boesch 2002, Dixit and Brylinsky 2008). A simple model was developed, based on loading and tidal exchange, which represented a theoretical nitrogen concentration in estuaries. Model outputs were then compared to estuary response variables in order to determine appropriate nitrogen loading criteria. The CSCR concept is illustrated in Figure 10, where:

Q_o is the rate of inflow of oceanic water at nitrogen concentration N_o

Q_f is the rate of inflow of freshwater at nitrogen concentration N_{gw}

Q_e is the rate of outflow of estuarine water at nitrogen concentration N_e

The principal of *Conservation of Volume* was also adopted, for which it assumed that on average, estuary volume is not changing (Figure 10). This can be written as:

$$Q_o + Q_f = Q_e \qquad (2)$$

It was also assumed that a steady state exists in each estuary such that the mass of nitrogen entering the estuary is equal to that leaving the estuary (Figure 10). This represents a highly simplified approach that also ignores any biological processes and nutrient sinks or reservoirs which may exist within each estuary. This assumption can be written as:

$$Q_o * N_0 + Q_f * N_{gw} = Q_e * N_e \qquad (3)$$

Making use of these two assumptions, the change in nitrogen concentration that theoretically occurs in the estuary as a result of the anthropogenic load can be written as:

$$\Delta N = N_e - N_0 = (Q_f * (N_{gw} - N_0)) / (Q_o + Q_f) \qquad (4)$$

Or, if $N_{gw} >> N_0$, that is that the fresh water nitrogen concentration is much greater than the oceanic concentration as is the case in PEI, as:

$$\Delta N \sim L / (Q_o + Q_f) \qquad (5)$$

Where:

ΔN (Delta-N) is the difference between the nitrogen concentration of the oceanic water and the estuarine water and represents a theoretical nitrogen concentration present in the estuary (averaged over the 6 month period from May to October).

L is loading to the estuary and

$\mathbf{Q_o}$ and $\mathbf{Q_f}$ are as given above

As **ΔN** becomes larger, it is assumed that there is an increased risk of eutrophication, high productivity and subsequent anoxia.

This proposed **ΔN** model can be easily explained in layman's terms; the **ΔN** represents the nitrogen concentration increase above oceanic values that would result if all water inflowing from the ocean into the estuary on the rising tide and all of the freshwater discharged into the estuary (including it's nitrogen load) over the six month period from May to October were thoroughly mixed in a container and then measured. It should be noted that $\mathbf{Q_f}$ is generally just a small proportion of $\mathbf{Q_o}$ and, in most cases, has a negligible impact on the final result.

2.5 Model Outputs and Criteria Development

Formula 5 was used to calculate **ΔN** values for the thirty-four estuaries used in this exercise. Model inputs and outputs are shown in Table 2. Model output (**ΔN**) is also shown in Figure 11.

The **ΔN** values produced appear diagnostic of anoxic events (Figure 11). Anoxic estuaries generally had higher **ΔN** values than non-anoxic estuaries (Figures 11 and 12, Table 2). Statistical comparison of **ΔN** values was performed using Systat 10. The log transformed values for the anoxic and non-anoxic estuaries were normally distributed and had equal variance (Levene's test, $p = 0.295$). The **ΔN** values were significantly higher for anoxic than for non-anoxic estuaries (two sample t test, $p = 0.005$; Figure 12). There was, however, considerable overlap in the **ΔN** values of anoxic and non-anoxic estuaries (Figures 11 & 12).

Visual examination of the data indicates that there were several possible cut off points in the **ΔN** values that distinguish between anoxic and non-anoxic estuaries. Of these a value of 0.06 appears to be the most appropriate as it provided the least overlap between anoxic and non-anoxic estuaries. Fifteen of twenty estuaries with at least one known anoxic event had **ΔN** values above 0.06 while eleven of fourteen estuaries with no known anoxic events had **ΔN** values below this value (Figure 11, Table 2).

The CCME guidance on the development of nutrient criteria advocates the use of the reference condition approach (CCME 2007) in which estuaries or near shore areas with pristine or un-impacted conditions are used to define the criteria using a quartile approach. The 75^{th} percentile of causal variable is considered to be protective of eutrophication in un-impacted estuaries (CCME 2007). Alternatively,

in the absence of un-impacted sites the 25th percentile of a mixture of impacted and un-impacted sites may also be used (CCME 2007). The median Delta-N value of all 34 estuaries is 0.0618 while the 25th percentile of the 20 estuaries with at least one recorded anoxic event is 0.0579 and the 25th percentile of **ΔN** values of all north shore estuaries, which are the most impacted region of the province in terms of anoxic events, is 0.0615.

Theoretically **ΔN** values above 0.06 would indicate an increasing tendency toward anoxia (Figure 11). Ten of eleven estuaries with a **ΔN** value above 0.10 are known to have undergone at least one anoxic event, while only five of sixteen estuaries with **ΔN** values below 0.06 are known to have had anoxic events.

The range of **ΔN** of 0.06 to 0.10 is the range in which anoxic events are most likely to occur. An **ΔN** above 0.10 indicates that anoxic events are almost certain to occur. This range can be considered a critical **ΔN** range (Figure 11).

2.6 Validation of Critical ΔN Range

Validation of the **ΔN** critical range of 0.06 to 0.10 is possible using data from the PEI Estuaries Survey. Measured concentrations of both nitrate and total nitrogen were generally below the analytical method detection limits of 0.02 mg/L and 0.50 mg/L at both the middle and outer estuary stations.

Despite being generally above the detection limits there was little correspondence between **ΔN** and the forms of nitrate measured at the upper station of each estuary ($r^2 = 0.152$, $p = 0.162$ for nitrate and $r^2 = 0.451$, $p < 0.001$ for total nitrogen). This was not surprising as the output produced by the model can, as previously stated, be viewed as a theoretical concentration that would only be present in the estuary if the model assumptions are met and the biology and processes are turned off.

A regression analysis of dissolved oxygen saturation, expressed as the variance observed in annual readings measured over the last 10 years, versus the **ΔN** values for each estuary produces a strong relationship ($r^2 = 0.806$, $p < 0.001$; Figure 13). All eight estuaries with a dissolved oxygen variance above 1500 (which equates to 38.7% saturation) have had at least one anoxic event since 2002. Seven of these eight estuaries have **ΔN** values above 0.06 of which six have a **ΔN** above 0.1 (Figure 13). Of the thirteen estuaries with a variance in dissolved oxygen saturation below 1500 only six have had anoxic events and only three have **ΔN** values above 0.06. None are above a **ΔN** value of 0.1 (Figure 13).

These results support the use of **ΔN** as a predictor of dissolved oxygen problems at the upper station of each estuary. In fact, variance in dissolved oxygen saturation may provide a better endpoint for the current model than the presence or absence of anoxic events. It should be noted, however, that a significant amount of data would be required to determine a dissolved oxygen variance for

any particular site while the occurrence of anoxic events is more readily identified.

Regression analysis also revealed that **ΔN** values were related to chlorophyll levels recorded at the upper estuary station ($r^2 = 0.657$, $p < 0.001$; Figure 14). Thirteen of fourteen anoxic estuaries had chlorophyll-a values above 10 µg/L while only one of seven non-anoxic estuaries had chlorophyll-a values above this concentration (Figure 14). There was no relationship between **ΔN** and chlorophyll at the middle estuary station ($r^2 = 0.227$, $p < 0.001$) despite anoxic estuaries having a higher mean chlorophyll concentration overall (Figure 7).

DISCUSSION

There is very good correspondence between **ΔN** values and observed conditions of anoxia in the thirty-four estuaries for which **ΔN** values have been calculated. Twenty six of the thirty-four estuaries have values that match their current designation of being either anoxic or non-anoxic based on the observation of at least one anoxic event in these estuaries over the last ten years.

Only eight of the thirty-four estuaries had **ΔN** values that did not match the designated anoxic condition. Five had **ΔN** values below 0.06 but reported anoxic events at least once over the last ten years (Brudenell River estuary, Boughton River estuary, Cardigan River estuary, Souris River estuary and Covehead Bay); and three had **ΔN** values above 0.06 but no reported anoxic events in the same timeframe (Brae River estuary, North Lake Creek and Tryon River estuary; Figure11, Table 2). Measurements from the annual PEI Estuaries Survey confirmed that increasing **ΔN** values correspond to increasing variance in dissolved oxygen concentration (Figure 13) and increasing chlorophyll concentration (Figure 14).

One possible explanation for differences between the calculated **ΔN** values and observed conditions in estuaries is undocumented anoxic events. Some of the modeled estuaries (Brae River, North Lake Creek, Tryon River, Morell River, Barbara Weit River and Indian River) could have had anoxic events which have gone unobserved or unreported. This alone would explain over half of the discrepancies between and the anoxic response observed.

It is difficult to imagine that anoxic events could go un-noticed in PEI as they are usually met with quite a bit of concern from the public. A typical public response to an observation of an event is to contact government staff. There is also a network of these staff across the province on the lookout for such events. Anecdotal information would seem to suggest that people are less likely to contact officials if anoxia is becoming routine, however, as the local population can become complacent to its reoccurrence.

Currently the frequency, extent and intensity of anoxic events are not considered; the primary response variable was the presence/absence of anoxia. It is possible that anoxic events that cover a larger geographic area could occur in estuaries

with a higher **ΔN** value. Likewise anoxic events that occur more frequently and/or that last a longer time could possibly be related to higher **ΔN** values. Currently only limited data on the extent or duration of anoxic events is collected. If available, this type of data might provide additional interpretation of **ΔN** values.

Another possible source of discrepancy between **ΔN** values and estuary condition are violations of the **ΔN** model assumptions. The **ΔN** model is applicable to Prince Edward Island estuaries because they generally have small freshwater discharges compared to tidal volumes and are generally small and shallow. As a result they tend to be well mixed (not stratified) satisfying the assumptions of the CSCR upon which the model is based. Estuaries which do not fit these general characteristics may have the least agreement between **ΔN** values and observed estuary conditions.

As an example, the Morell River estuary is long and narrow and has a high freshwater to oceanic water inflow ratio (0.36:1). It may behave more like a fresh water system than an estuary. The high volume of fresh water in the system may be an additional source of oxygen that could counteract the effects of high loading on dissolved oxygen levels and lower susceptibility to anoxic events. The other thirty three estuaries included in this exercise have an average fresh to oceanic water inflow of 0.03:1. The 2nd highest ratio is only 0.06:1. As a result, the Morell River estuary may not fit the **ΔN** model.

Stratification could also be an issue in some estuaries. Cardigan and Boughton rivers both have had anoxic events despite very low **ΔN** values (Table 2, Figure 11). Both estuaries are known to be stratified; Cardigan River has a bridge at the upper end of the estuary which can result in an occasional salt wedge, and occasional anoxia, in deep upstream areas; Boughton River is generally deep and stratified in the upper estuary at all times and has annual anoxic events. Other anoxic estuaries with low **ΔN** values (Brudenell, Covehead and Souris) may also be stratified in the upper estuary (Figure 15). However, they are no more stratified (as identified by current monitoring) than several other similar estuaries (Trout/Stanley River, Murray River, Montague River and Southwest River) which appear to fit the model well (Figure 15, Figure 11).

Additional reasons for some estuaries not fitting the current model are related to the calculation of the principal model components; loading and flushing. Currently, loading calculations are made from predicted base-flow concentrations multiplied by freshwater flows. Large watersheds have large freshwater flows, so in large watersheds even small inaccuracies in the base-flow nitrate concentration can be greatly magnified. Table 1 shows watershed sizes for all 34 estuaries studied in this exercise. Three of the largest watersheds in the exercise were St. Peter's Bay, Dunk River and Montague River. All three had **ΔN** values which did not match the magnitude of biological response noted in the estuary.

Estuary loading calculations may not be complete as not all nitrogen sources were considered. For example, the current calculations do not consider animal manures as a nitrogen source in the watershed. For many estuaries this may not be an issue as livestock operations may represent only a small fraction of total

inputs and livestock manures may already be captured in the nitrogen accounting used in the model.

In some other watersheds livestock operations may represent a much larger portion of land use and manures may be treated more as a waste product than a nitrogen resource. In watersheds such as these animal manures may be applied in amounts beyond normal nitrogen application rates (Barry Thompson, PEI Department of Agriculture, personal communication, 2012). If this is the case certain livestock rich watersheds may have additional nitrogen sources that are not accounted for in the current model.

Approximately half of the estuaries and bays modeled in this exercise flow directly to the Northumberland Strait or the Gulf of St. Lawrence. The others flow into coastal bays. Nitrogen contributions from the boundary waters are not currently considered in the model since offshore waters are considered to contribute a negligible nitrate load in comparison to watershed sources. This may not be the case in bays where nitrate concentrations could be somewhat higher than from offshore waters due to nitrogen loading from point sources or other tributaries and watershed areas. In some estuaries this load could be significant, resulting in higher Δ**N** values overall. Estuaries that have significant nitrogen contributions from boundary waters would be more susceptible to nitrogen loading from their watersheds overall.

Since freshwater inflows represent, in most cases, only a small fraction of the total inflow used in the model, issues with the flushing part of the Δ**N** calculation may be related to inaccuracies in the oceanic inflow estimation. These estimations were made using estuary surface areas drawn from a 2000 series of orthophotos. A more recent orthophoto series, with higher resolution, may make coastal features more visible and allow for a more accurate representation of estuary surface area which could result in small changes to some Δ**N** values.

In addition, some estuary flushing characteristics may not be fully captured by the model as only the amount of inflowing tide is currently considered. In PEI estuaries located on the north and south eastern shores generally have very small inter-tidal areas with very little area of tidal flats exposed at low tides. Large tidal flats on the south shore are more common, especially in upper estuary areas. This likely represents a more complete exchange of nutrients from upper estuary with the lower estuary or offshore waters, with high nutrient waters from the upper estuary being removed on a low tide and replaced with lower nutrient waters on a rising tide. This could be addressed by developing and utilizing a correction, called tidal skew, to the model calculations which would capture the degree to which an estuary drains or remains filled with water at low tide.

The configuration of the bays and estuaries studied may also be a factor. Estuaries that are broad and shallow (e.g. Covehead Bay and Brackley Bay) could be more susceptible to *Ulva* growth due to a greater area of the estuary being within the photic zone. This could result in higher productivity over the surface area of both bays with smaller nitrogen loads. Data on *Ulva* productivity is currently not available as capturing *Ulva* productivity has proven problematic,

particularly in highly eutrophic or severely anoxic estuaries that may experience several cycles of *Ulva* growth and die-off during a season. Having *Ulva* productivity available would provide an additional response variable with which **ΔN** values could be validated.

The contributions of other nutrients or nitrogen fractions have not been considered at this time. There is some evidence that the Boughton River may be more responsive to phosphorus than nitrogen loads. A case study provided by the CCME (2007) indicated that the Boughton River was phosphorus limited and that anoxic events could be reduced by keeping estuary phosphorus levels below a trigger level. The current exercise does not investigate this possibility as the model used is currently for nitrogen (and in particular nitrate) only.

CONCLUSIONS AND RECOMMENDATIONS

As part of efforts to develop nitrogen criteria for estuaries a simple loading model, based on the principle of a Continuously Stirred Chemical Reactor, has been developed for Prince Edward Island. Nitrate loading and flushing characteristics for thirty four Island estuaries have been used to calculate values (**ΔN** or Delta-N) that represent the theoretical nitrate concentration which would exist in each estuary in the absence of biology and other processes.

Although very simple, the **ΔN** model has several notable attributes that make it useful tool for Prince Edward Island. It requires data that is readily available and unlike other possible calculations results in a parameter that is easily converted to a nitrate loading target, through the determination of a threshold value for eutrophication for all similar estuaries and then using the estuary flushing characteristics to calculate the threshold's corresponding load. It is a calculation of average exchanges (over the six month period from May to October) that ignores the episodic changes in nitrate concentration that can occur in an estuary. As biology and other processes are ignored, it is a calculated characteristic of an estuary which is not meant to represent any real or measurable estuary nitrate concentration.

The model shows remarkably good correspondence to the oxic condition of most of the thirty four estuaries to which the model was applied; twenty-five of thirty-four estuaries had **ΔN** values which correctly indicated whether these estuaries had experienced any anoxic events in the ten years between 2002 and 2011. Chlorophyll and dissolved oxygen data from the PEI Estuaries Survey have been used to validate model outputs and confirm these findings.

Nine estuaries and bays produced **ΔN** values which did not match the designated anoxic condition observed in these estuaries. There are a number of possible explanations for these apparent exceptions including:

- Undocumented anoxic events;

- The use of a binary response variable (anoxia either present or not present) does not provide enough validation of **ΔN** values; capturing the extent and duration of anoxic events may provide a more continuous response variable which could aid in further interpretation of **ΔN** values;
- Violation of model assumptions including relatively high freshwater influence and the presence of stratification in certain estuaries;
- Inaccuracies in the calculation of estuary loading and flushing components;
- Estuary flushing characteristics, such as tidal skew, not captured by the current model;
- Estuary configuration or area available for *Ulva* growth;
- Possibility of phosphorus limitation.

These issues may be resolved with further data collection and or refinements in methodology. It is recommended that, until this is done, the current model be adopted as an interim method to calculate interim nitrate loading guidelines to address anoxic events in PEI estuaries. Use of the interim guidelines produced by this methodology should be restricted to cases where the result appears consistent with local expert opinion of the known estuary condition.

The use of these interim guidelines will permit stakeholders to begin development nitrogen loading targets for watersheds which consider the economic and social costs of implementing the land-use changes required to meet a certain water quality condition. This, in the case of this method, would reflect a certain probability of anoxic events occurring.

The model output demonstrated that the onset of periodic anoxia most likely occurs when **ΔN** is between 0.06 and 0.10. Below 0.06, anoxic events appear to be less likely and above 0.1 they appear to be almost certain. It is recommended that the development of nitrate loading targets could consider that anoxic events are more likely to occur with increasing **ΔN** values as follows:

ΔN Value	**Possibility of Anoxic Event(s)**
<0.06	Possible, but unlikely
0.06	Likely, especially for estuaries located within a coastal bay
0.08	Very likely
>0.10	Almost certain

Values of **ΔN** from within this range can be used for particular estuaries on a per case basis, as a management tool to determine the nitrate load which results in the best achievable water quality.

The ΔN value which is chosen as a target for a particular estuary may be used to calculate a target watershed nitrate load as follows:

$$L_{tar} \sim \Delta N_{tar} * (Q_o + Q_f) \quad (6)$$

Where:

L_{tar} is the target nitrate load to the estuary for May to October

ΔN_{tar} is the ΔN value that produces the minimum acceptable possibility of anoxia in the estuary

Q_o is the volume of oceanic entering the estuary between May and October

Q_f is the volume of freshwater entering the estuary from the watershed between May and October

This calculated target load could then be used in a watershed or groundwater model (similar to LEACHN used in this exercise) to determine the amount or degree of change in watershed activities that would have to be carried out to prevent anoxic events from occurring in this estuary. This could then be used in watershed planning activities, such as nutrient management, within this watershed.

The PEI Department of Environment, Labour and Justice has conducted a preliminary assessment of target loads calculated by this methodology which indicates that in some impacted estuaries significant changes in land use may be required to reduce or eliminate the occurrence of anoxic events in Island estuaries. Reductions in nitrate loading of over 50% are indicated in several estuaries (Table 3). Changes of this magnitude go well beyond what may be achievable by the implementation of best management practices and would have a considerable impact on all human activities in the watershed.

NEXT STEPS

The next steps should focus on refining the current methodology to help explain the currently observed discrepancies from the model output:

- Additional data on the physical characteristics of PEI estuaries should be collected. This could include the inclusion of tidal skew in model calculations and the collection of additional or new data on estuary surface area, bathymetry, stratification and the potential *Ulva* growing area (based on photic zone) for each estuary. These could be incorporated into a refined model as sufficient data is collected.
- Certain estuaries that do have few or no known anoxic events and which do not fit the model output results (such as North Lake Creek, Barbara Weit River, Indian River, Morell River, Brae River and Tryon River) should

be investigated for the presence of anoxic conditions and/or dissolved oxygen impairment.

- Additional detail on reported anoxic events should be collected. This would include both the spatial extent and temporal duration of each event.
- Additional data should be collected so that additional response variables can be considered. For example, values for *Ulva* productivity should be collected. *Ulva* productivity could be an indicator used to validate **ΔN** values or to measure impacts of nitrogen loading reductions.
- Manure inputs to nitrogen loading should be included for each estuary.
- Modelled nitrogen loads from the outer boundary of each estuary should be incorporated into the current model rather than considering these as a negligible load. It is suggested that the current model might be suitable for this purpose.

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Table 1. Nitrate loads estimated using land use based area weighted approach. Total loads used in the nitrogen criteria model also included point sources such as municipal wastewater or industrial effluents. Estuaries highlighted in red have had at least one known anoxic event since 2001.

Estuary/Bay	Code	Watershed Area	Predicted Average NO_3-N Conc.	Area-Weighted NO_3-N Load	Predicted Summer* NO_3-N Load	
		km^2	(mg/l)	kg/Ha/Year	kg/day	kg (10^4)
Brudenell River estuary	BDR	5.60	2.76	11.82	163.66	3.01
Brackley Bay	BRA	3.07	2.67	11.21	85.96	1.58
Brae River estuary	BRE	1.54	3.51	14.73	48.63	0.89
Boughton River estuary	BRR	9.36	1.75	7.33	148.13	2.72
Barbara Weit River estuary	BWR	2.40	5.25	46.96	293.65	5.40
Cardigan River estuary	CAB	8.29	1.41	5.94	121.38	2.23
Trout/Foxley River estuary	CAS	9.04	3.58	15.88	296.53	5.45
Souris River estuary	COL	4.85	2.88	10.82	126.80	2.33
Covehead Bay	COV	4.24	2.72	11.60	121.38	2.23
Enmore River estuary	ENM	4.54	1.03	4.32	42.07	0.77
Flat River/Gascoigne Cove	FLA	3.06	1.18	4.95	37.35	0.69
Freeland River estuary	FRE	0.93	1.48	6.20	12.40	0.23
Grand River estuary	GDR	11.74	2.54	10.75	273.90	5.04
Hillsborough River estuary	HBR	27.97	1.86	7.83	539.75	9.93
Indian River estuary	IND	2.59	5.56	23.34	149.20	2.75
Kildare/Montrose River estuary	KIL	5.54	5.03	21.12	251.33	4.62
Montague River estuary	MGR	19.65	2.42	10.67	519.44	9.56
Mill River estuary	MIR	11.65	3.85	16.15	479.54	8.82
Morell River estuary	MOR	17.03	1.92	8.05	338.14	6.22
Murray Harbour estuary	MUR	7.11	1.27	5.37	94.13	1.73
Trout/Stanley River estuary	NLB	8.64	2.63	10.65	235.41	4.33
North Lake Creek	NLC	5.11	1.29	5.41	59.68	1.10
North River estuary	NOR	7.49	2.59	12.27	229.40	4.22
Orwell/Vernon River estuary	ORB	9.71	2.04	8.55	204.76	3.77
Pinetter River estuary	PIN	5.85	1.81	7.60	109.67	2.02
Wheatley River estuary	RUS	6.14	3.01	12.64	216.29	3.98
St. Peters Bay	SPB	31.51	2.12	3.95	606.38	11.15
Dunk River estuary	SSH	21.17	5.55	23.42	1,222.70	22.50
Southwest River estuary	SWR	3.84	5.34	22.44	212.56	3.91
Tracadie Bay	TRB	13.29	1.95	5.87	268.30	4.94
Tryon River estuary	TRY	5.53	5.03	21.12	287.69	5.29
West River estuary	WES	18.67	2.22	9.76	471.73	8.68
Wilmot River estuary	WIL	8.73	6.70	28.14	605.75	11.15
Winter River estuary	WIN	7.17	2.26	9.50	171.64	3.16

* Summer refers to the growing season for *Ulva* (May to October) for which the models were developed

Table 2. Calculated Delta-N (ΔN) values for thirty four estuaries in Prince Edward Island showing model inputs (estuary size, tides and estimated N loads). Total Tidal Amplitude and Total Summer Tidal Inflow values given in bold italics are taken from offshore tidal models while the tide values in regular text are from measured tides. Rows highlighted in red are estuaries known to have had one or more anoxic events since 2001. ΔN values in bold italics indicate a discrepancy between the ΔN value and the occurrence of reported anoxic events (either a low ΔN and reported anoxia or a high ΔN and no reported anoxia).

Estuary	Code	Total Summer* NO_3.N Load kg (10^4)	Estuary Surface Area km^2	Total Tidal Amplitude m	Summer* FW Discharge (Qf) m^3 (10^7)	Total Summer* Tidal Inflow (Qo) m^3 (10^9)	Ratio (Qf / Qo)	Delta-N
Brudenell River	BDR	3.01	3.67	300.1	1.09	1.10	0.010	***0.027***
Brackley Bay	BRA	1.58	2.80	84.5	0.59	0.24	0.025	0.065
Brae River	BRE	0.89	0.39	141.9	0.25	0.05	0.045	***0.156***
Boughton River	BRR	2.72	9.44	267.1	1.72	2.52	0.007	***0.011***
Barbara Weit River	BWR	5.40	1.02	162.1	0.60	0.17	0.036	0.315
Cardigan River	CAB	2.23	8.84	300.1	1.61	2.65	0.006	***0.008***
Trout/Foxley River	CAS	5.45	2.24	140.2	1.44	0.31	0.046	0.192
Souris River	COL	2.33	2.04	243.3	0.89	0.50	0.018	***0.048***
Covehead Bay	COV	2.23	4.84	109.3	0.82	0.53	0.016	***0.042***
Enmore River	ENM	0.77	2.45	***130.2***	0.72	***0.32***	0.023	0.024
Flat River	FLA	0.69	0.62	***439.9***	0.59	***0.27***	0.022	0.025
Freeland Creek	FRE	0.23	0.39	***163.5***	0.15	***0.06***	0.023	0.035
Ellis (Grand) River	GDR	5.04	9.96	165.2	1.87	1.64	0.011	0.030
Hillsborough River	HBR	9.93	17.37	***494.6***	5.42	***8.59***	0.006	0.011
Indian River	IND	2.75	0.63	***156.2***	0.50	***0.10***	0.051	0.264
Kildare River	KIL	4.62	2.16	91.7	0.88	0.20	0.045	0.223
Montague River	MGR	9.56	4.90	300.1	3.81	1.47	0.026	0.063
Mill River	MIR	8.82	4.23	141.4	1.86	0.60	0.031	0.143
Morell River	MOR	6.22	0.92	98.8	3.30	0.09	0.363	0.502
Murray River	MUR	1.73	4.59	***297.2***	1.38	***1.36***	0.010	0.013
Trout/Stanley River	NLB	4.33	2.58	150.3	1.67	0.39	0.052	0.107
North Lake Creek	NLC	1.10	1.10	***157.3***	0.94	***0.17***	0.054	**0.060**
North River	NOR	4.22	1.92	***494.6***	1.45	***0.95***	0.015	0.044
Orwell Bay	ORB	3.77	2.97	***443.7***	1.88	***1.32***	0.014	0.028
Pinette River	PIN	2.02	5.08	***468.4***	1.13	***2.38***	0.005	0.008
Wheatley River	RUS	3.98	1.41	133.5	1.19	0.19	0.063	0.176
St. Peter's Bay	SPB	11.15	15.50	97.5	6.11	1.51	0.040	***0.071***
Dunk River	SSH	22.50	8.27	***311.6***	4.10	***2.58***	0.016	0.086
Southwest River	SWR	3.91	2.38	147.7	0.74	0.35	0.021	0.109
Tracadie Bay	TRB	4.94	15.61	123.5	2.86	1.93	0.015	0.026
Tryon River	TRY	5.29	1.20	***507.1***	1.07	***0.61***	0.018	***0.085***
West River	WES	8.68	4.71	***494.6***	4.46	***2.33***	0.019	0.037
Wilmot River	WIL	11.15	3.24	***311.6***	1.69	***1.01***	0.017	0.109
Winter River	WIN	3.16	3.14	122.6	1.67	0.38	0.043	0.079

* Summer refers to the growing season for *Ulva* (May to October) for which the models were developed.

Table 3. Loading reductions required for the modeled estuaries using various values as ΔN_{tar}. Estuaries highlighted in yellow have had at least one reported anoxic event since 2001.

Estuary	Code	Modelled ΔN	Loading Reduction Required (ΔN_{tar} =0.06)	Loading Reduction Required (ΔN_{tar} =0.08)	Loading Reduction Required (ΔN_{tar} =0.10)
Brudenell River estuary	BDR	0.027	None	None	None
Brackley Bay	BRA	0.065	8.0%	None	None
Brae River estuary	BRE	0.156	61.5%	48.7%	35.9%
Boughton River estuary	BRR	0.011	None	None	None
Barbara Weit River estuary	BWR	0.315	81.0%	74.6%	68.3%
Cardigan River estuary	CAB	0.008	None	None	None
Trout/Foxley River estuary	CAS	0.192	68.8%	58.3%	47.9%
Souris River estuary	COL	0.038	None	None	None
Covehead Bay	COV	0.042	None	None	None
Enmore River estuary	ENM	0.024	None	None	None
Flat River estuary	FLA	0.025	None	None	None
Freeland Creek estuary	FRE	0.035	None	None	None
Grand River estuary	GDR	0.030	None	None	None
Hillsborough River estuary	HBR	0.011	None	None	None
Indian River estuary	IND	0.264	77.3%	69.7%	62.2%
Kildare River estuary	KIL	0.223	73.1%	64.1%	55.2%
Montague River estuary	MGR	0.063	5.3%	None	None
Mill River estuary	MIR	0.143	58.1%	44.1%	30.1%
Morell River estuary	MOR	0.502	88.0%	84.1%	80.1%
Murray River estuary	MUR	0.013	None	None	None
Trout/Stanley River estuary	NLB	0.107	43.9%	25.2%	6.6%
North Lake Creek estuary	NLC	0.060	0.4%	None	None
North River estuary	NOR	0.044	None	None	None
Orwell Bay estuary	ORB	0.028	None	None	None
Pinette River	PIN	0.008	None	None	None
Wheatley River	RUS	0.176	65.9%	54.6%	43.2%
St. Peter's Bay	SPB	0.071	15.5%	None	None
Dunk River estuary	SSH	0.086	30.1%	6.8%	None
Southwest River estuary	SWR	0.109	44.9%	26.6%	8.2%
Tracadie Bay	TRB	0.026	None	None	None
Tryon River estuary	TRY	0.085	29.6%	6.1%	None
West River estuary	WES	0.037	None	None	None
Wilmot River estuary	WIL	0.109	44.8%	26.4%	8.0%
Winter River estuary	WIN	0.079	23.8%	None	None

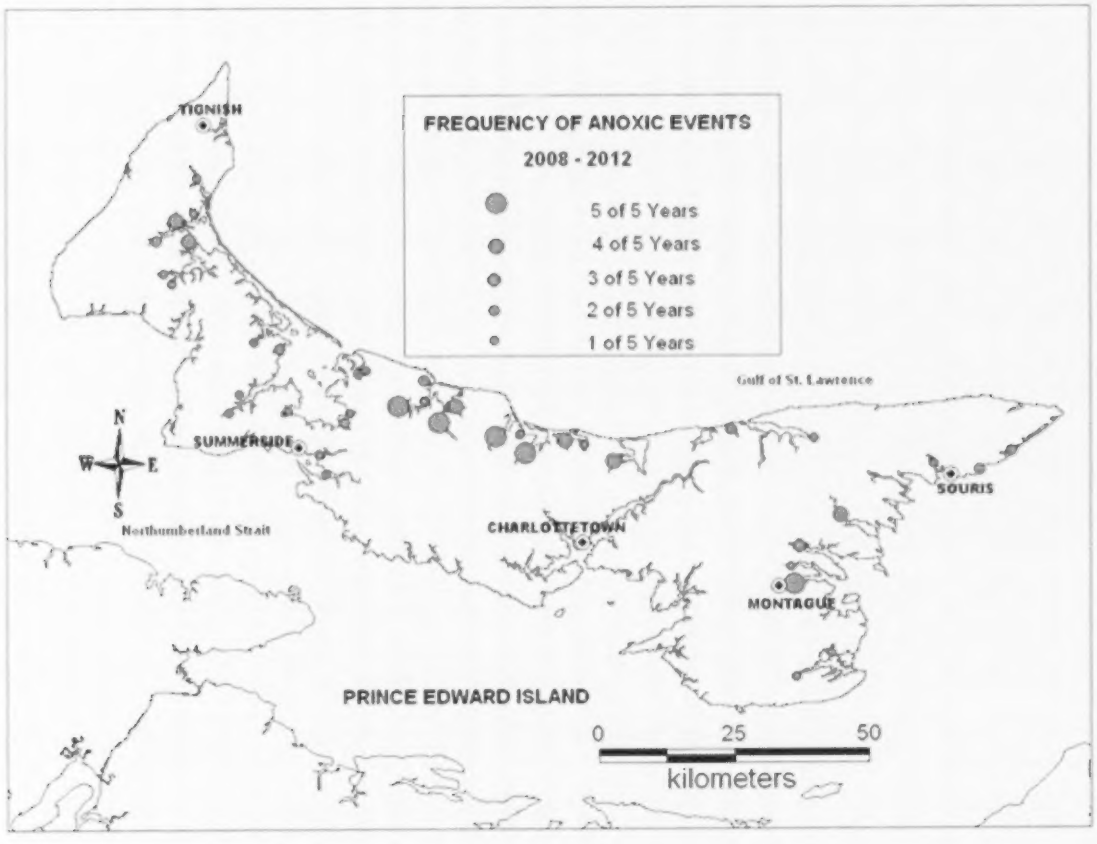

Figure 1: Estuaries and bays in Prince Edward Island which had anoxic events reported, 2008 - 2012.

Figure 2: Anoxic event in the Southwest River estuary, Prince Edward Island. June, 2009.

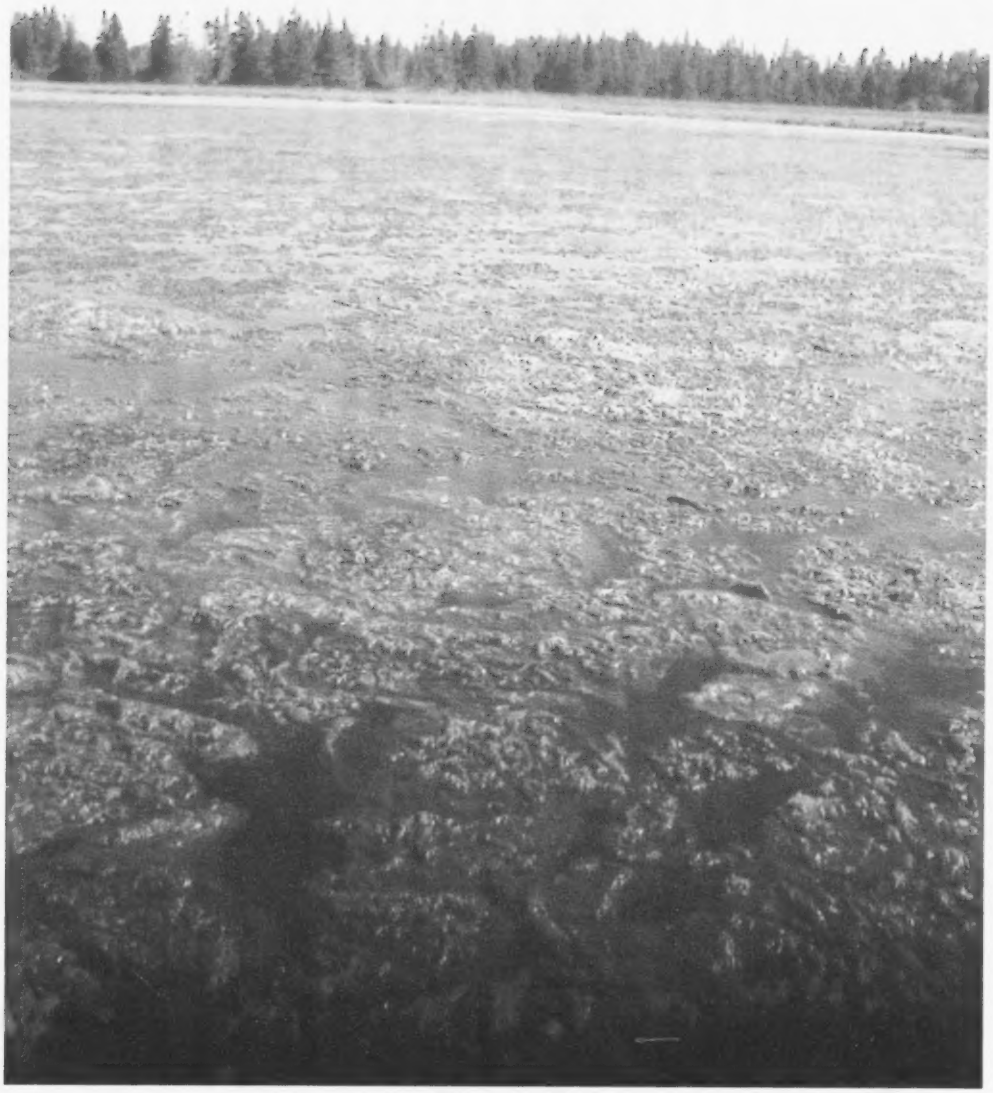

Figure 3: Prolific *Ulva* (sea lettuce) growth in the Barbara Weit River estuary, Prince Edward Island August 2009.

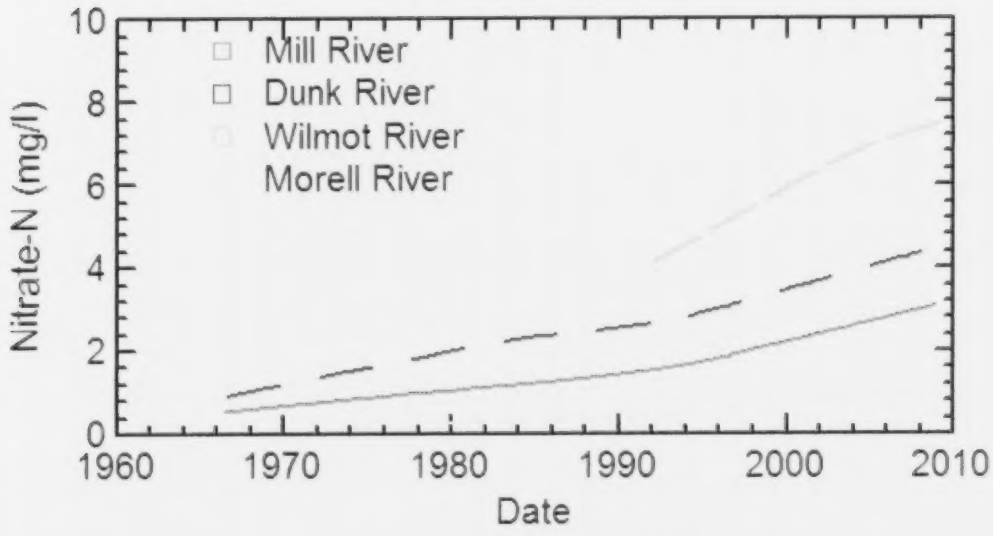

Figure 4: Nitrate trends in four freshwater streams in Prince Edward Island 1966 to 2008.

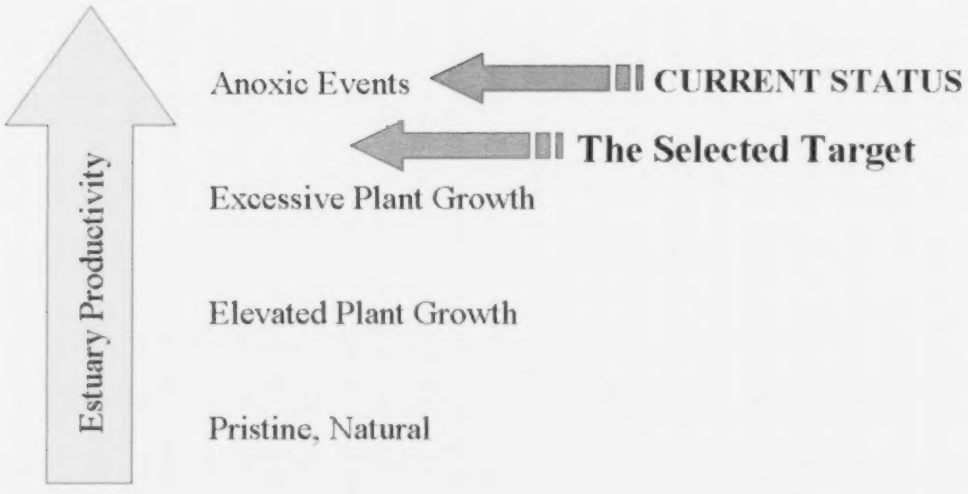

Figure 5: The estuary target concept used by the PEI RTAG to identify target water quality conditions used in this exercise. The selected target corresponds to a nitrogen loading value, specific to each estuary, which would eliminate or greatly reduce the occurrence of anoxic events.

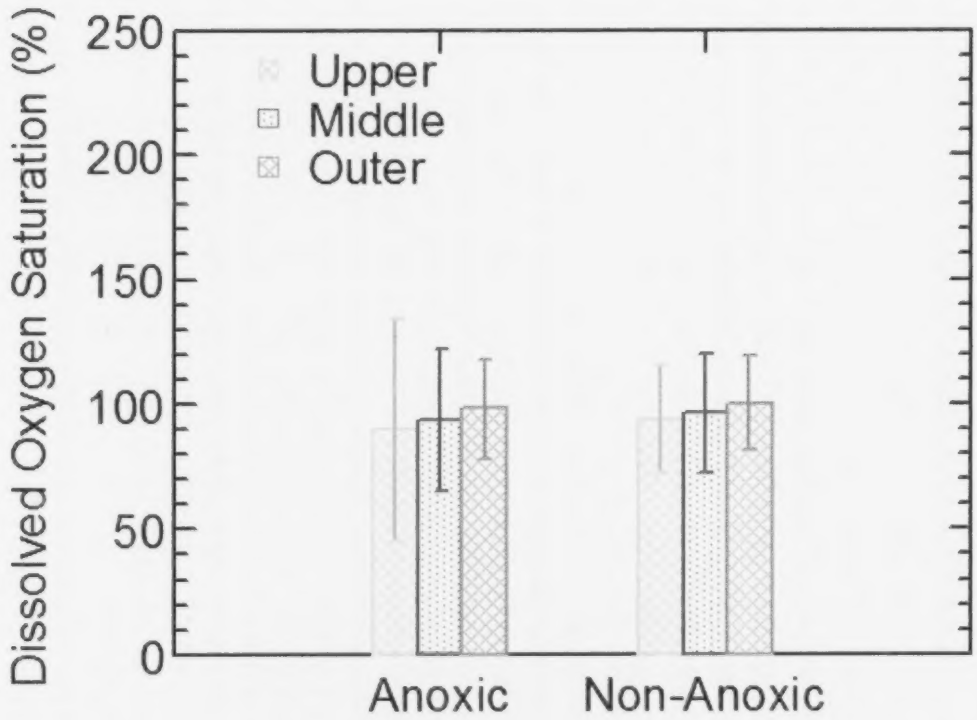

Figure 6: Mean dissolved oxygen saturation values for twenty one estuaries in the PEI Estuaries Survey (2002-2011) with at least one anoxic event (anoxic) and with no reported anoxic events (non-anoxic). The error bars shown are one standard deviation.

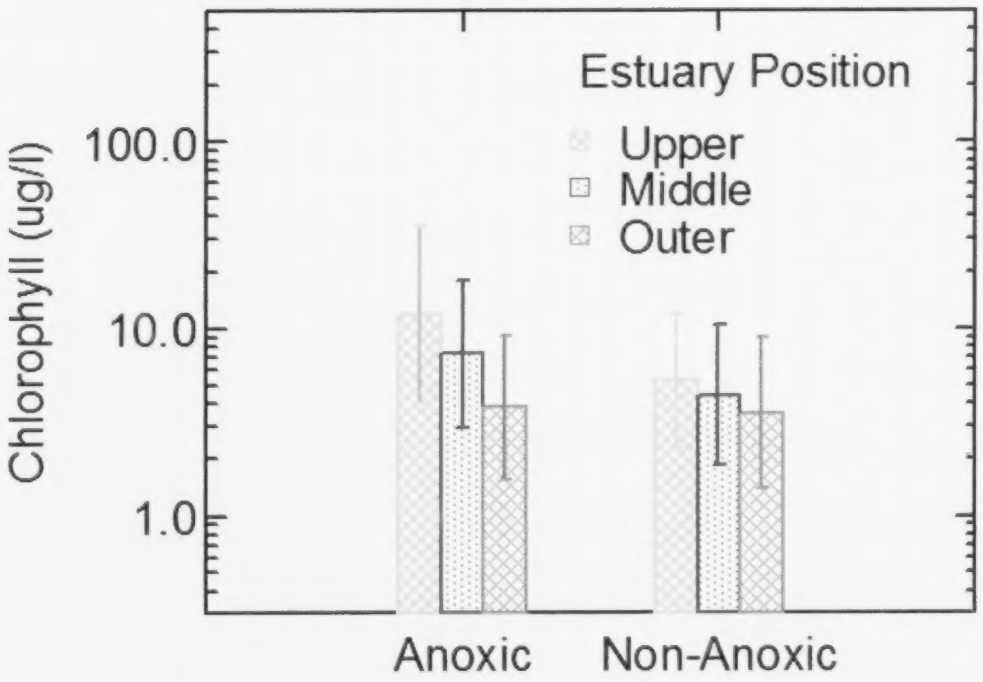

Figure 7 Mean chlorophyll values for twenty one estuaries in the PEI Estuaries Survey (2002-2011) with at least one anoxic event (anoxic) and with no reported anoxic events (non-anoxic). The error bars shown are one standard deviation.

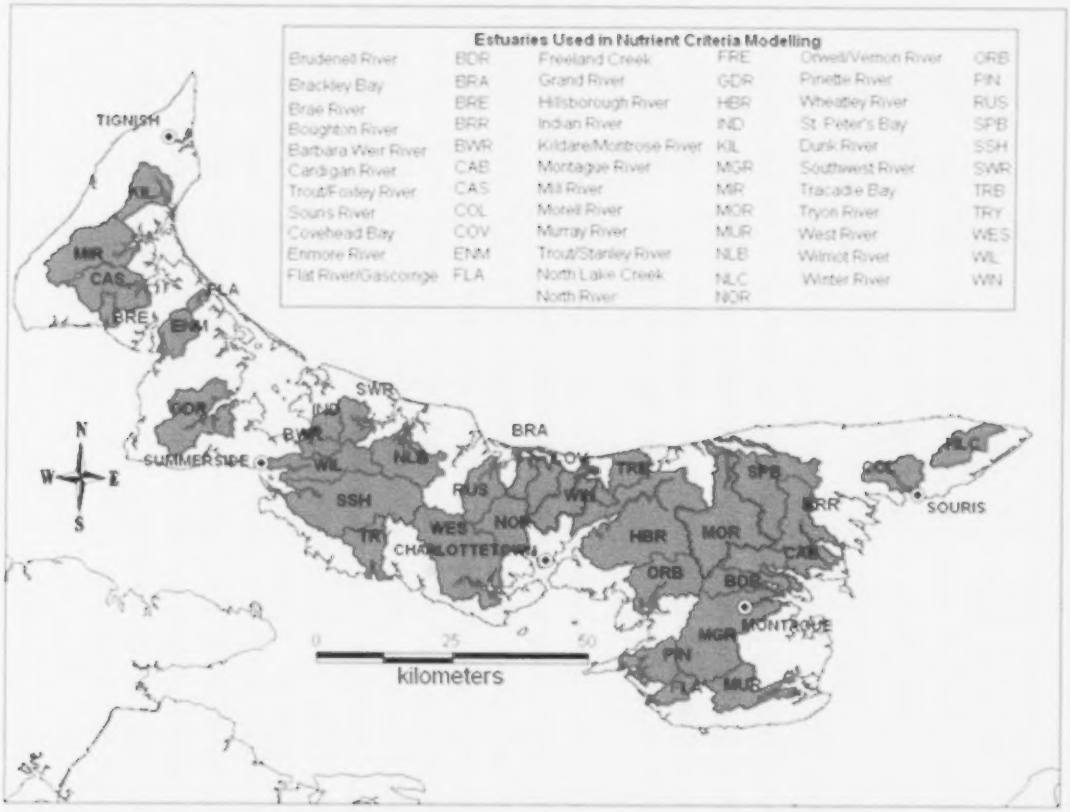

Figure 8: Watershed areas modeled in the present study.

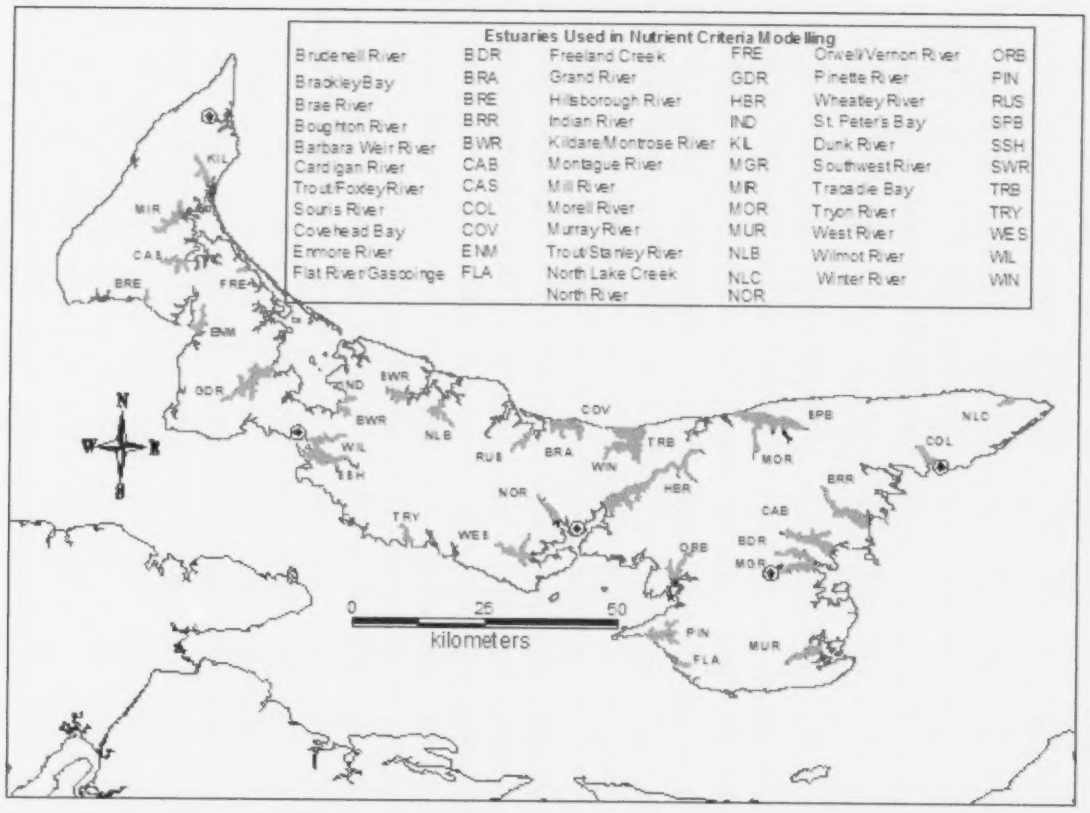

Figure 9: Estuary areas modeled in the present study.

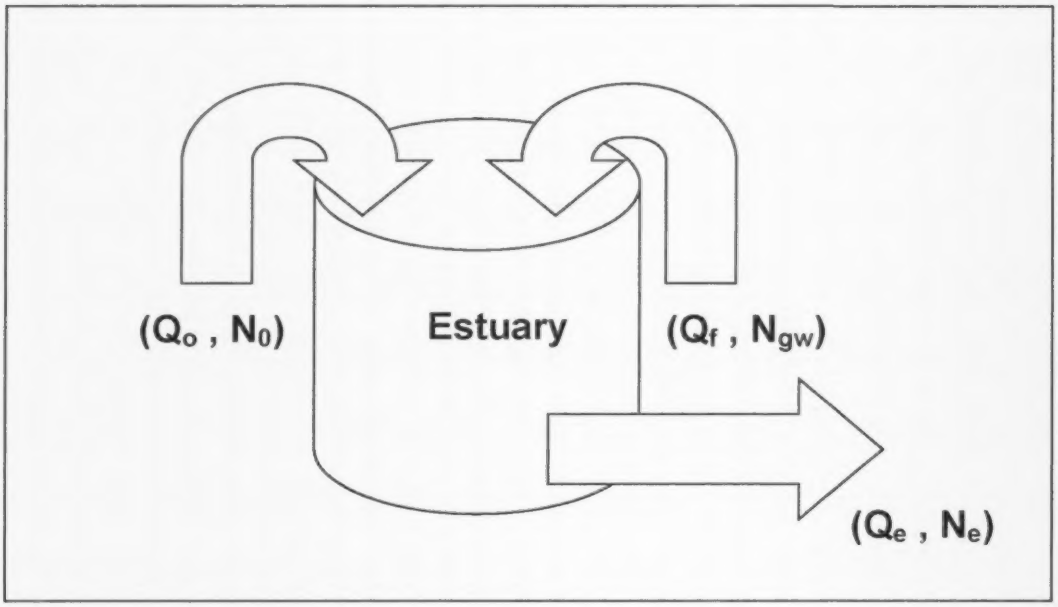

Figure 10: Conceptual diagram of a simple estuary model illustrating the assumptions of conservation of volume and steady state. Q_o and N_o are the oceanic water inflow and nitrogen concentration, Q_f and N_{gw} are the freshwater inflow and nitrogen concentration, and Q_e and N_e are the estuary water outflow and nitrogen concentration.

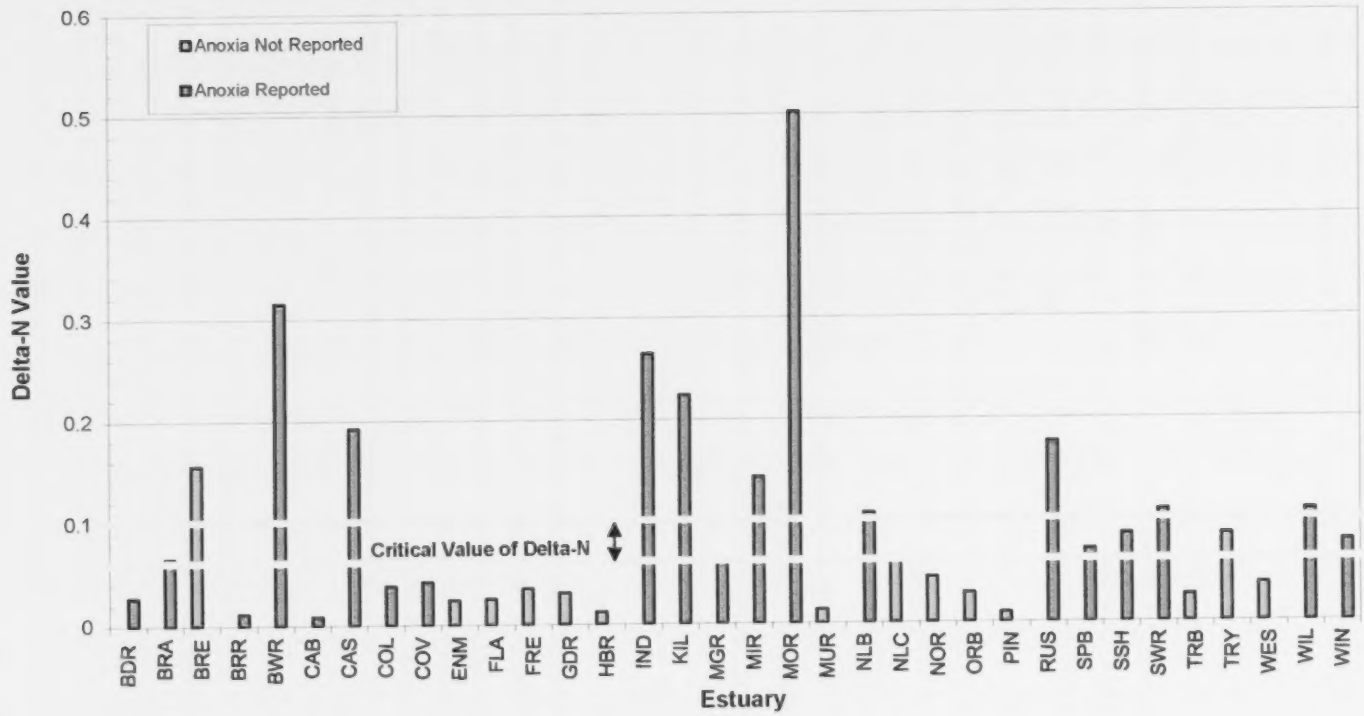

Figure 11: Delta N (ΔN) values for the thirty four estuaries examined in this exercise. Estuaries with at least one incidence of an anoxic event are shown in red while estuaries with no reported anoxic events are shown in blue. The key to the estuary codes found here are shown in Tables 1 and 2 and Figure 9.

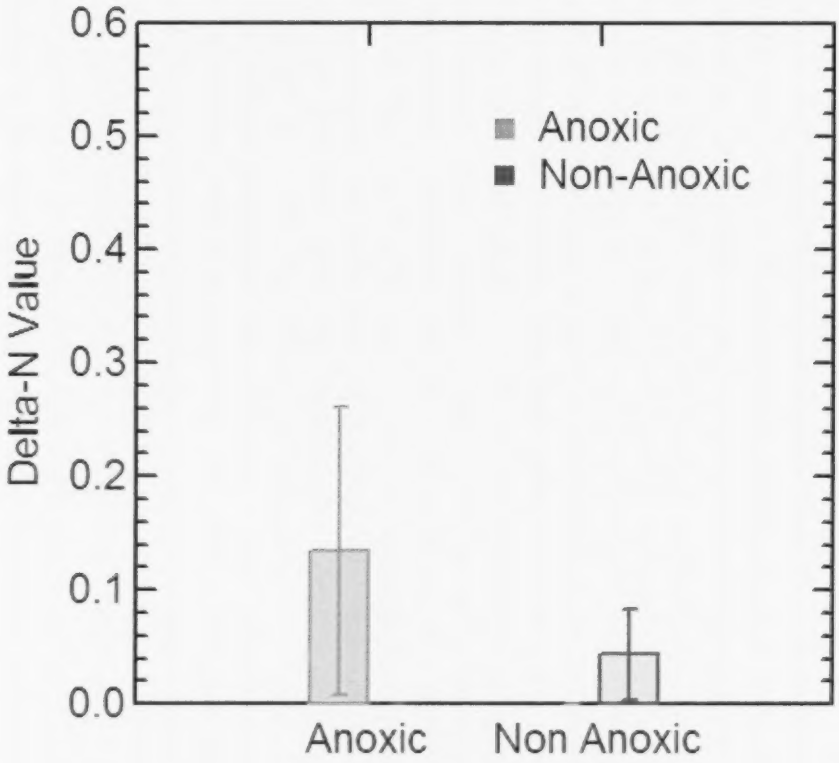

Figure 12: Mean Delta-N values for estuaries with at least one incidence of an anoxic event (Anoxic) and those with no known incidences of anoxia (Non-anoxic). The Anoxic estuaries have significantly higher ΔN values than Non-anoxic estuaries (two sample t test, $p = 0.005$). The error bars shown are one standard deviation.

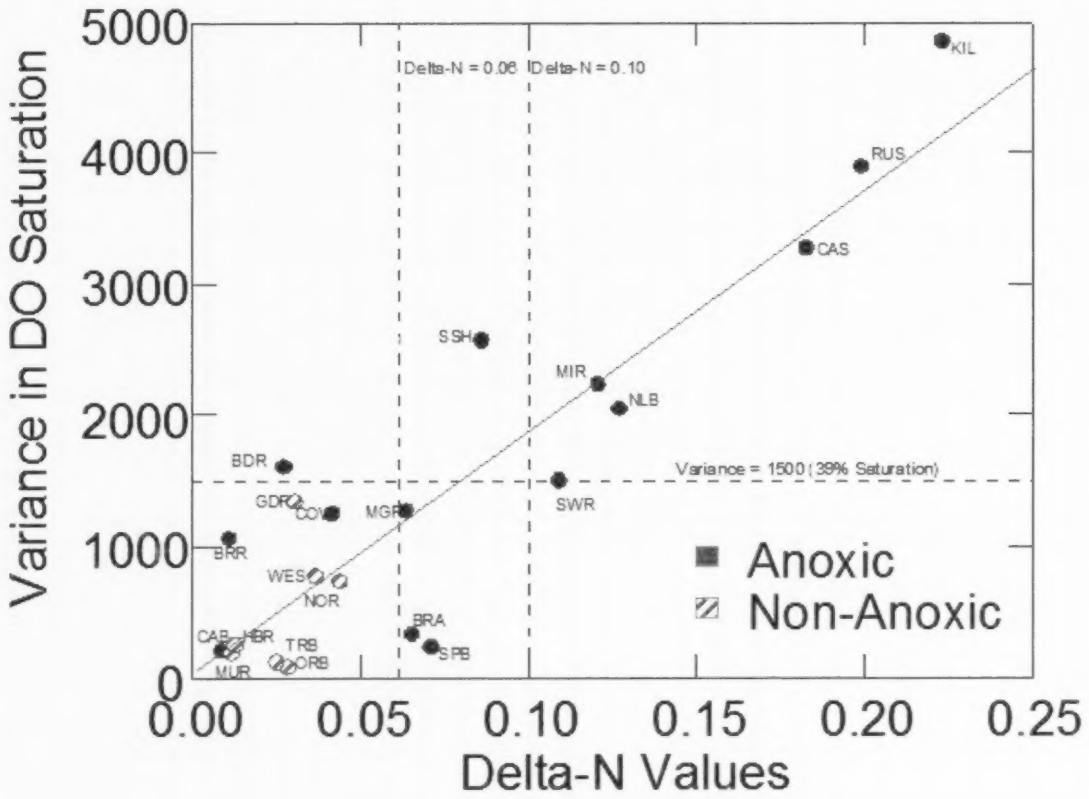

Figure 13: Relationship of **ΔN** (Delta-N) values to the variance in dissolved oxygen saturation (see text for details) ($r^2 = 0.806$, $p < 0001$).The vertical dashed lines represent the critical range of **ΔN** of 0.06 to 0.10 above which anoxic events are most likely to occur. See Tables 1 and 2 for estuary names.

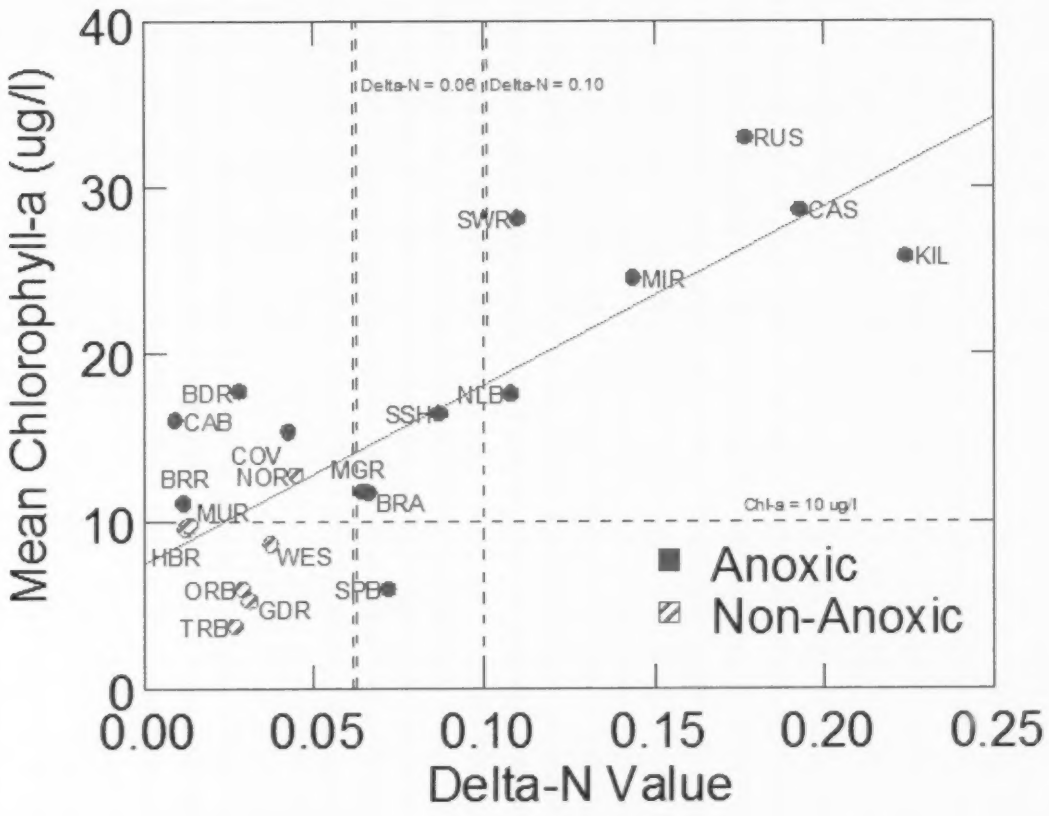

Figure 14: Relationship of **ΔN** (Delta-N) values to mean chlorophyll levels recorded at the upper estuary station (see text for details) (r^2 = 0.657, p =<0.001). The vertical dashed lines represent the critical range of **ΔN** of 0.06 to 0.10 above which anoxic events are most likely to occur. See Tables 1 and 2 for estuary names.

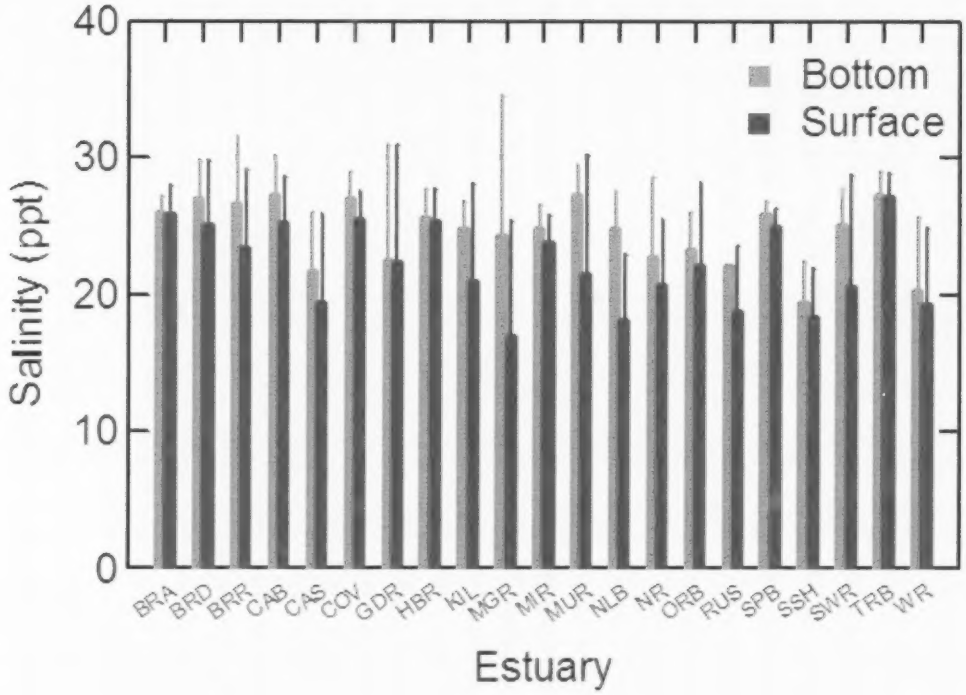

Figure 15: Mean salinity at the upper station of selected Island estuaries. Data is from the PEI Estuaries and was collected between 2002 and 2011. Data from mid and low tide stages were excluded. Error bars are one standard deviation.